



Research Article

Cu/ZnO/Al₂O₃/Cr₂O₃/CeO₂ Catalyst for Hydrogen Production by Oxidative Methanol Reforming via Washcoat Catalyst Preparation in Microchannel Reactor

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Received: 28th February 2017; Revised: 2nd May 2017; Accepted: 3rd May 2017;
Available online: 27th October 2017; Published regularly: December 2017

Abstract

The oxidative methanol reforming reaction was carried out using Cu/ZnO/Al₂O₃/Cr₂O₃/CeO₂ (15/15/2.5/1.25/1.25 mol%), with washcoat by EC sol on microchannel reactor. The experimental conditions were used various sol for washcoat of catalyst, various method for calcinations of catalyst, steam to methanol mole ratio, the mole ratio of oxygen to methanol, weight hourly space velocity, reaction temperature. The experiment result shows that methanol conversion achieved 98.8 % and carbon monoxide concentration equal to 1204 ppm when using Cu/ZnO/Al₂O₃/Cr₂O₃/CeO₂ (15/15/2.5/1.25/1.25 mol%) catalyst mixed with EC sol at the reaction temperature of 200 °C. Copyright © 2017 BCREC Group. All rights reserved

Keywords: Oxidative Methanol Reforming; Hydrogen; Microchannel Reactor; Washcoat; Cu/ZnO/Al₂O₃/Cr₂O₃/CeO₂

How to Cite: Lesmana, D., Wu, H.S. (2017). Cu/ZnO/Al₂O₃/Cr₂O₃/CeO₂ Catalyst for Hydrogen Production by Oxidative Methanol Reforming via Washcoat Catalyst Preparation in Microchannel Reactor. *Bulletin of Chemical Reaction Engineering & Catalysis*, 12 (3): 384-392 (doi:10.9767/bcrec.12.3.966.384-392)

Permalink/DOI: <https://doi.org/10.9767/bcrec.12.3.966.384-392>

1. Introduction

The fuel cell technology is considered as an attractive alternative because of its environmental compatibility and high energy conversion efficiency. Among the various types of fuel cells, polymer electrolyte fuel cell (PEMFC) systems are widely studied for portable electric devices because PEMFC provides the necessary specific power, power density and durability to

replace lithium-ion batteries. Although there is a trouble to store and transport hydrogen, it is preferred for portable PEM fuel cell. Furthermore, it is difficult to make small hydrogen storage tanks for application in portable PEMFC. Therefore, onboard fuel processing is an inevitable choice [1].

Technology for converting methanol into a hydrogen-rich supply for the fuel cells is mainly based on steam reforming, partial oxidation or a combination of both, namely oxidation steam reforming or oxidation reforming or autothermal reforming, in which the methanol oxidation reforming is the most promising way due to its en-

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ergy saving, fast start-up and quick response of the whole system. Due to thermodynamic constraints of methanol reforming, significant amount of CO as a poisoning impurity of platinum electro-catalyst is produced. It is also necessary to reduce the level of CO in the hydrogen-rich gas to less than 50 ppm, although high CO-resistant electrocatalysts were developed, so the process of preferential oxidation of CO is required [2].

Microchannel reactors are much more suitable for the distributed production of hydrogen compared to conventional systems with typical channel widths of 100-1000 μm , the large surface-to-volume ratios in these reactors lead to good heat and mass transfer properties and hence process intensification. Microchannel reactors work under laminar flow conditions demonstrating low-pressure drop compared to randomly fixed bed. The short radial diffusion time in gas phase leads to narrow residence time distribution of gases. This allows optimizing the contact time of reactors avoiding the formation of unwanted by-products. Moreover, the short residence time allows a quick response to dynamic changes in the inlet conditions. For non-stationary operations of the reactor, this feature is essential [3].

In the microchannel, the catalyst incorporation onto the microchannel is difficult. The preparation procedure is influenced by low interactions between metallic reactor surfaces and catalyst slurries [4]. Several coating techniques have been applied for microchannels such as chemical vapor deposition, anodic oxidation, sol-gel process, washcoating, and electro-deposition [5]. The wash-coating method is commonly used for this application [6]. The washcoat method has some advantages to obtain the utmost performance for the SRM reaction based on the resulting porosity and surface structures. The binder play a major role on the basis of: (i) slurry viscosity being affected by its chemical structure and molecular weight, (ii) coating adhesion, and (iii) catalytic activity by re-dispersion of the active phase because formation of metal complexes influences the catalytic activities in the WGS reaction [4].

The goal of this study was to immobilize the catalyst of $\text{Cu/ZnO/Al}_2\text{O}_3/\text{Cr}_2\text{O}_3/\text{CeO}_2$ (15:15:2.5:1.25:1.25 mol%) for methanol oxidation reforming on the wall of the stainless steel channels. In this paper, we report the methods to immobilize the catalyst in microchannels and to show potential miniaturization of microreactor used in the hydrogen generation system via methanol oxidative reforming. The catalysts were prepared by wash coat method with

Ethyl Cellulose (EC) sol as a binder.

2. Experimental

2.1 Materials

Methanol (99 %, Mallinckrodt, American), copper nitrate-2.5-hydrate (99 %, R.D.H, Germany), zinc nitrate-6-hydrate (99 %, R.D.H, Germany), aluminium nitrate-9-hydrate (99 %, J.T. Baker, American), chromium nitrate-6-hydrate (99 %, R.D.H, Germany), cerium nitrate-6-hydrate (99 %, R.D.H, Germany), oxalic acid (99 %, R.D.H, Germany), EC sol (99 %, Alfa Aesar, American) and other reagents are all expanded chemicals.

2.2 Microchannel reactor setup

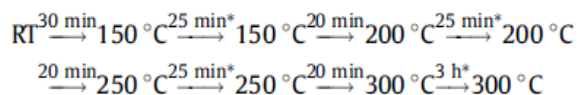
Microchannel in this microreactor were made of the special used stainless steel with a flow route of reactants and products. The size of the plate with microchannel was 35 (L) \times 25 (W) \times 0.5 (T) mm. The plate was designed with 14 microchannels with the plate of 20 (L) \times 10 (W) \times 0.2 (D) mm. Methanol, water and air were passed through the right or left upper inlet and were distributed over the plates sequentially to the parallel microchannels. Finally, H_2/CO_2 mixtures were collected through the outlet at the bottom. A graphite gasket was used between microchannel plates for gastight and the whole reactor was contained in stainless-steel housing.

2.3 Catalyst wash coat preparation

The preparation of catalysts was reported in our previous study [7,8,9]. Catalyst-precursor solutions were prepared by adding $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}(\text{s})$ (11.7 g), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}(\text{s})$ (11.7 g), $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}(\text{s})$ (2.56 g), $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}(\text{s})$ (0.43 g), and $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}(\text{s})$ (0.90 g) into flasks containing ethanol (100 mL, -5°C), and the solutions were stirred until the compounds dissolved. Each precursor solution was reacted with 20 % excess oxalic acid. The initial pH of the precursor solution was measured to be 0.4 by using a pH meter (SP-701, Suntex, Taiwan). The precipitate ($\text{Cu/ZnO/Al}_2\text{O}_3/\text{Cr}_2\text{O}_3/\text{CeO}_2$ (42.9:42.9:7.14:3.57:3.57 wt.)) was mixed with 50 %vol of the (ethyl cellulose) EC sol as a binder to enhance the adhesion between precursor slurry and the microreformer.

After, stainless steel substrate surfaces were cleaned with acetone/ $\text{HNO}_3(\text{aq})$ and then the precursor slurry was washcoated on the surface of microchannels followed by calcined under O_2 at a flow rate of 100 mL/min, by ap-

plying a programmed temperature regime [8] as depicted in Scheme 1, in which the time marked with “*” is holding time, and the others are heating time, in which the time marked with “*” is holding time, and the others are heating time.



Scheme 1. Programmed temperature regime

After calcination, the precipitates were ground into solid plate catalyst in microchannel. The catalyst materials were then reduced in a stream of 10 % H_2/N_2 at a flow rate of 100 mL/min, and at an initial temperature of 25 °C and final temperature of 300 °C at a heating rate of 5 °C/min for 3 h. The catalyst properties were characterized using ChemBET TPR/TPD (Quantachrome Instrument model, American) to compare the reproducibility of the fresh catalyst. Next, 0.1 g of sample was placed in a quartz fixed bed reactor, and 30 mL/min a high-purity flow of 10 vol% H_2 -Ar mixtures (TPR) was passed through the bed. The temperature of sample was raised at a rate of 5 °C/min from 30 °C up to 400 °C and the composition of hydrogen was monitored by means of TCD cell in GC (Shimadzu 8A) and the results were recorded with a computer [7].

2.4 Catalyst activity measurement

The experimental apparatus used in this study was conducted in a lab-scale five-plate microchannels reactor using washcoat catalysts. The performance of methanol conversion tests were conducted in a lab-scale one-plate microchannels reactor using washcoat catalysts. After the catalyst was applied in one plate, the total weight of as-synthesized catalyst coated on the one plate was 0.5 mg. Weight of plate measured in before and after reaction to controlled the weight of catalyst used electronic balanced (Mettler, Switzerland, AE100).

The plate was then placed in housing and heated by isolated type heated. The temperature was controlled by a microprocessor-based temperature controller through a K-type thermocouple. The reaction temperature was measured at outlet of housing.

The mixture of methanol and water, which had a molar ratio of water/methanol (W/M) 1.2, was introduced to an evaporator through a syringe pump at a rate of 2.4 cm^3/h . Air flow to an evaporator by 20 sccm. This mixture (water, methanol and air) was then heated to evaporate to the gas phase after passing through an evaporator. All runs were conducted at an atmospheric pressure and at a selected temperature of 200 °C. The reactive tube from the outlet of the reactor was also heated with electric heating tape to prevent condensation of the compounds in the gas [8,9].

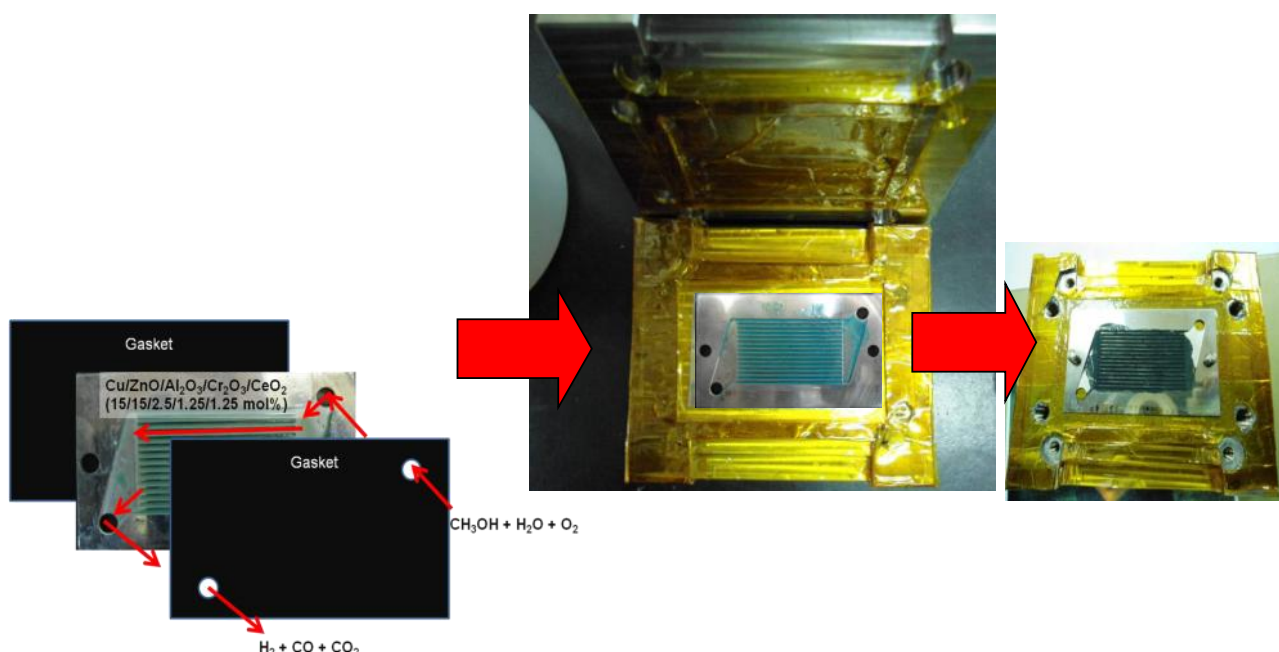


Figure 1. Schematic diagram for typical oxidative reforming methanol in microchannel reactor

The mixture gas was carried to a microchannel reactor by 20 (sccm) air flow, and the weight hourly spaced velocity (WHSV) operated at 6.22 h^{-1} . Methanol and water were condensed in a condenser with isopropanol of 33 mL. Then the liquid was collected to determine the methanol content using a gas chromatograph (Shimadzu 14B, Japan) with a flame ionization detector, carrier gas of nitrogen as a mobile phase ($30 \text{ cm}^3/\text{min}$), hydrogen as a detector gas ($0.9 \text{ kg}/\text{cm}^2$) and air ($0.6 \text{ kg}/\text{cm}^2$). Column: 7HK-G013-22 ZB-WAX, Length 30 m, I.D. 0.53 mm, film $1 \mu\text{m}$ and temperature range of $45 \text{ }^\circ\text{C}$ to $75 \text{ }^\circ\text{C}$. The sample was withdrawn at a selected time interval of 1 h [8,9].

The concentrations of H_2 , CO, and CO_2 were measured using a gas chromatograph (Shimadzu 8A, Japan) with a thermal conductivity detector and a carrier gas of helium as a mobile phase ($30 \text{ cm}^3/\text{min}$), a molecular sieve 13X column, a Chromosorb 120 column, and temperature range of $100 \text{ }^\circ\text{C}$ to $160 \text{ }^\circ\text{C}$. The sample was withdrawn at a selected time interval of 1 h [8,9].

2.5 Mathematical equation used to measurement catalyst activity

The final compounds of this oxidative reforming reaction process were methanol (M), water (W), hydrogen (H_2), carbon monoxide (CO), and carbon dioxide (CO_2). Other by products was not detected in this work. Thus, X_M denote the methanol conversion and selectivity of carbon dioxide, V_{H_2} , and V_{CO} denotes the concentration of hydrogen and carbon monoxide, respectively.

$$X_M = \frac{C_{M,0} - C_{M,\text{unreacted}}}{C_{M,0}} \times 100\% \quad (1)$$

$$V_{\text{H}_2} = \frac{C_{\text{H}_2}}{C_{\text{total}}} \times 100\% \quad (2)$$

$$V_{\text{CO}} = \left(\frac{\frac{C_{\text{CO}} \times 100\%}{C_{\text{total}}} \right) \times 10^6 \quad (3)$$

The term $C_{M,0}$ denotes the initial concentration of methanol (kmol/m^3) as measured using gas chromatograph. C_{total} denotes the amount of concentration of H_2 , N_2 , CO_2 and CO . The production rate per weight of the catalyst r_{H_2} ($\text{mol}/\text{min.gcat}$) and molar flow rate F_{H_2} (mol/min) of hydrogen can then be expressed as:

$$r_{\text{H}_2} = \frac{F_{\text{H}_2}}{\text{weight of catalyst}} \quad (4)$$

and

$$F_{\text{H}_2} = (3 - \alpha) \cdot F_{\text{CH}_3\text{OH}} \cdot X_{\text{CH}_3\text{OH}}, 0 \leq \alpha \leq 1 \quad (5)$$

where α denotes the mole ratio of oxygen to methanol flow rate.

3. Results and Discussion

3.1 Characterization data of catalyst

Figure 2 (a) shows the hydrogen consumption profiles during temperature programmed reduction of the $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3/\text{Cr}_2\text{O}_3/\text{CeO}_2$ pre-

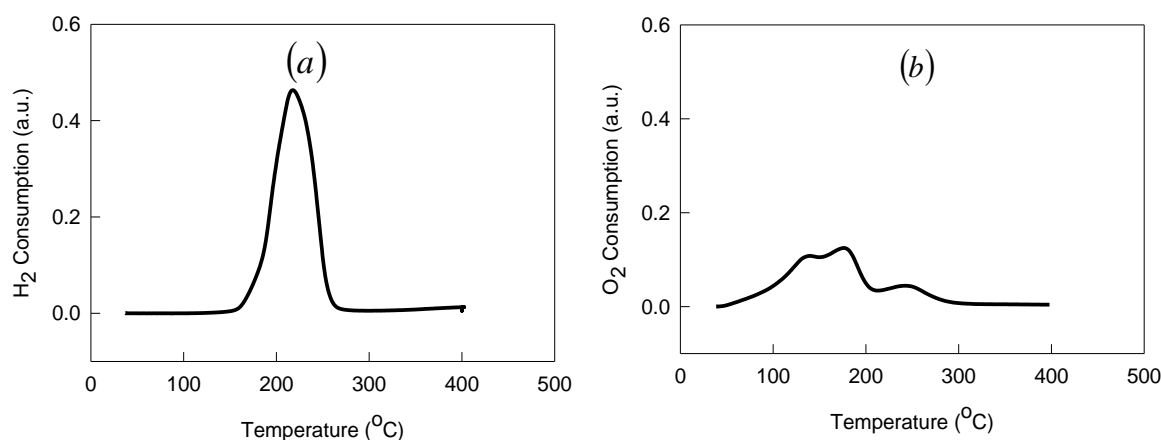


Figure 2. Temperature-Programmed Reduction (TPR) profiles of $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3/\text{Cr}_2\text{O}_3/\text{CeO}_2$ (15/15/2.5/1.25/1.25 mol%) catalyst (a); Temperature-programmed oxidation (TPO) profiles of $\text{Cu}/\text{ZnO}/\text{Al}_2\text{O}_3/\text{Cr}_2\text{O}_3/\text{CeO}_2$ (15/15/2.5/1.25/1.25 mol%) catalyst (b)

cursors. Oxide precursors showed an onset of reduction between 150 °C and 270 °C. The maximum of the reduction peaks obtained are located at about 210 °C.

Figure 2 (b) shows the oxygen interaction with Cu/ZnO/Al₂O₃/Cr₂O₃/CeO₂ precursors in oxidation profiles during temperature programmed oxidation. Oxide precursors showed an onset of oxidation between 40 °C and 300 °C. From Figure 2 (b), it looks that there are three peaks in figure. The first peak is a peak found in the medium temperature range from 120 °C to 150 °C. The second peak is the highest in temperature range from 150 °C to 210 °C. The third peak is the lowest peak on the temperature range from 210 °C to 290 °C. The highest peak is a peak of the interaction between oxygen and copper precursor. The highest peak that occurs at the 150 °C to 210 °C that can be interpreted as that on the catalyst can be easily oxidized.

3.2 Effect of calcinations method (In-situ and Ex-situ)

The author tries to prove that the method of calcination catalyst is very influential to the activity of the catalyst.

Figure 3 shows that calcinations at in-situ method better than ex-situ method. It is based on conversion methanol and hydrogen concentration higher at the catalyst prepared with in-situ calcinations than ex-situ calcinations. This is probably because after the process of in-situ calcinations, catalyst cannot contact with air (oxygen) so that the activity of the catalyst by in-situ calcination be higher than ex-situ calcination. Contact with air can decrease the activity of the catalyst, because the air is capable of oxidizing catalyst and the active phase covering most of the catalytic, so activity of the catalyst that makes being on the decline.

3.3 Effect of various sols as a binder on catalyst washcoat

The binder has plays a major role on the catalyst washcoat [4]. Binder served to reinforce coating adhesion between sols and catalyst in microchannel plate. Coating adhesion strength it can be correlated with the absence of a catalyst regardless or out of the plate on microchannel when before and after the reaction takes place. To prove this, author performs the measurement of microchannel plate on some condition (an empty plate, after wash-

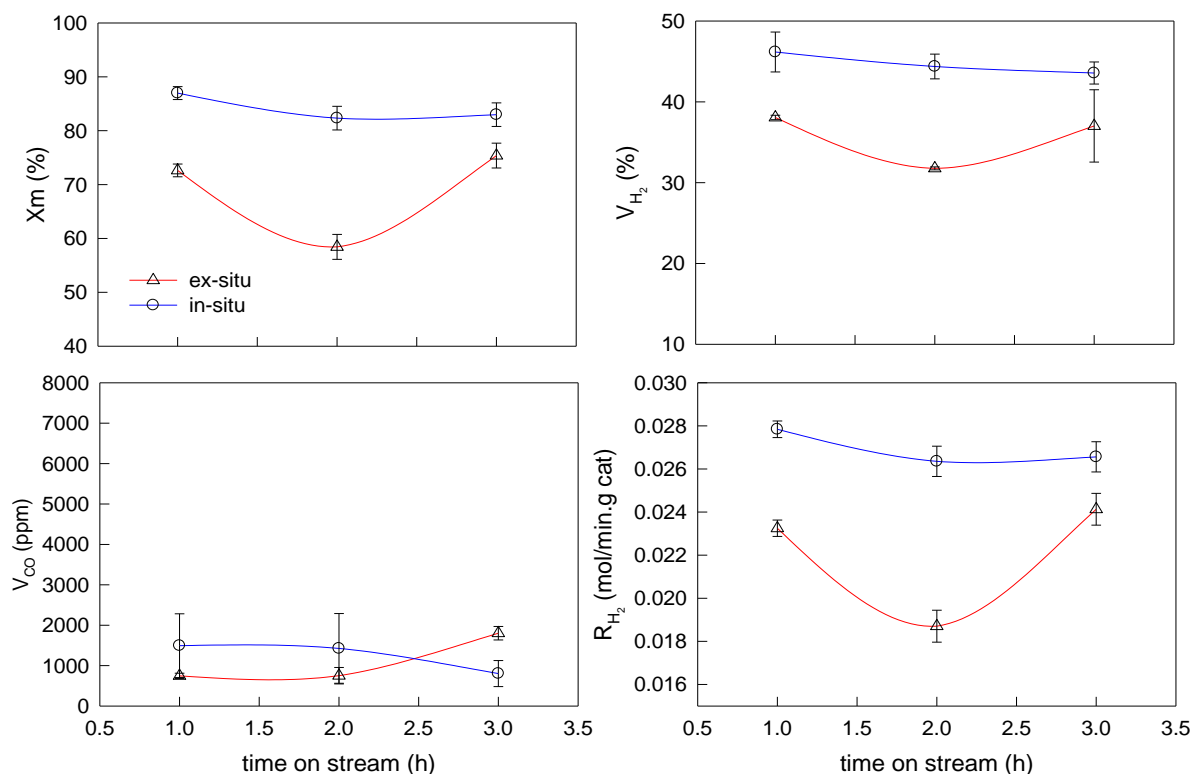


Figure 3. Cu/ZnO/Al₂O₃/Cr₂O₃/CeO₂ (15/15/2.5/1.25/1.25 mol%), CeO sols, washcoat method, Un-set pH (0.4), stirring 500 rpm (5 h), drying 50 °C (2 h), catalyst weight = 0.5 mg, W/M = 1.2, O/C = 0.27, WHSV = 6.23 h⁻¹, Reaction temperature = 200 °C

coat, after drying, after calcinations and after reaction). As shown in Table 1.

Table 1 shows that the catalyst mixed with EC sol it is better than without sol and mixed with CeO sol. It is based on the percentage of the loss of catalytic washcoat until after the reaction. These results have the same linear with the Figure 4. Figure 4 shows the activity of the catalyst on microchannel plate washcoat has done with different types of sol. Catalyst mixed with EC sol has a high activity compared to the catalyst mixed with CeO sol and catalyst without sol.

3.4 Effect of oxygen/methanol molar ratio (O/C) and WHSV

The operating condition of microchannel very impact on the performance of microchannel, several researchers have studied the effect of operating conditions on the performance of

microchannel [10].

Figure 5 shows that the higher molar ratio of O/C then the concentration of hydrogen on a product stream decreased, while the conversion of methanol O/C about 0.27 is a optimum condition. It is the same as reported by Yong *et al.* [11]. They are reported that methanol conversion increases with increasing molar ratio of O/C. However that the hydrogen production rate increases with decreasing molar ratio of O/C [11]. Increased molar ratio of O_2/CH_3OH in the feed, ATR reaction could be from endothermic to exothermic. Hence, it could offer an effective way to regulate the reaction temperature in the reactor, and less heat exchange between cold and hot streams is required. This makes the reformer compacter especially important for transportation fuel cell applications [12].

Table 1. Measurement the plate on microchannel

	Plate before washcoat (blank) (g)	After wash-coat (g)	After drying (g)	After calcination reduction (g)	After reaction (g)	Percentage of catalyst loss (%)
CeO ₂ sol	8.000	8.491	8.201	8.052	8.023	95.3
EC sol	8.000	8.494	8.234	8.066	8.048	90.3
Without sol	8.000	8.498	8.102	8.043	8.015	97

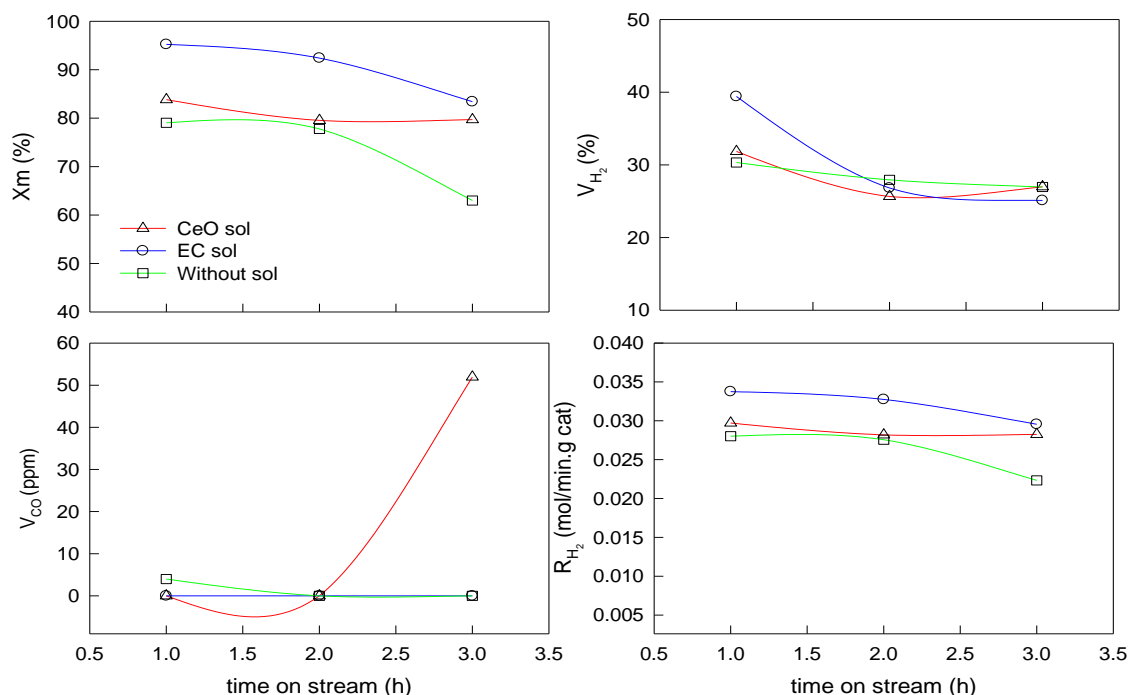


Figure 4. Cu/ZnO/Al₂O₃/Cr₂O₃/CeO₂ (15/15/2.5/1.25/1.25 mol%), washcoat method, un-set pH (0.4), stirring 500 rpm (5 h), drying 50 °C (2 h), catalyst weight = 0.5 mg, W/M = 1.2, O/C = 0.27, WHSV = 6.23 h⁻¹, reaction temperature = 200 °C.

Space velocity is also a crucial factor that can influence the catalyst activity and concentration profiles. Diffusion of reactant gas is often influenced by gas velocity, and surface reactions are generally influenced by contacting time of reactant species with catalysts. Increase of space velocity will increase gas velocity and promote mass transfer [13]. Figure 5 shows WHSV 6.21 h⁻¹ is better than 3.16 h⁻¹ and 1.61 h⁻¹. From Figure 5, increased WHSV can increase the methanol conversion and concentration of hydrogen on a product stream is also increased. Therefore, the WHSV about 6.21 h⁻¹ is an optimum condition.

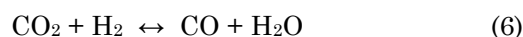
For operating conditions of WHSV 3.16 h⁻¹ and 1.61 h⁻¹, CO concentration on a product stream is very low so it can't be detected, it is the same as reported by Du *et al.* [10]. They are reported that the microchannel is a competitive technology to produce hydrogen at low temperatures (200-300 °C) and contributes to a low CO concentration in the outlet gases [10].

3.5 Effect of reaction temperature

The effect of reaction temperature on the performance of the microchannel reactor with the Cu/ZnO/Al₂O₃/Cr₂O₃/CeO₂ (15/15/2.5/1.25/1.25 mol%) catalyst is shown in Figure 6.

Methanol conversion and hydrogen concentration on product stream increase with increasing temperature.

The maximum methanol conversion is 98.9 % at 200 °C. In the temperature range of 180–200 °C, the CO concentration on product stream maximum at 1204 ppm with the minimum of 1069 ppm at 200 °C. CO is not a primary product during the reaction, many reports indicate that CO is produced by the reverse water shift reaction (Equation (1)) at a higher temperature [3].



4. Conclusions

Microchannels is a promising way to produce hydrogen via oxidative methanol reforming reaction with Cu/ZnO/Al₂O₃/Cr₂O₃/CeO₂ (15/15/2.5/1.25/1.25 mol%) catalyst. The catalyst mixed with EC sols, coating by washcoat method onto stainless steel plate and characterized by in-situ calcinations and reduction can perform on oxidative methanol reforming reaction on a microchannel reactor.

Space velocity is also a crucial factor that can influence the catalyst activity and concentration profiles. Methanol conversion increases

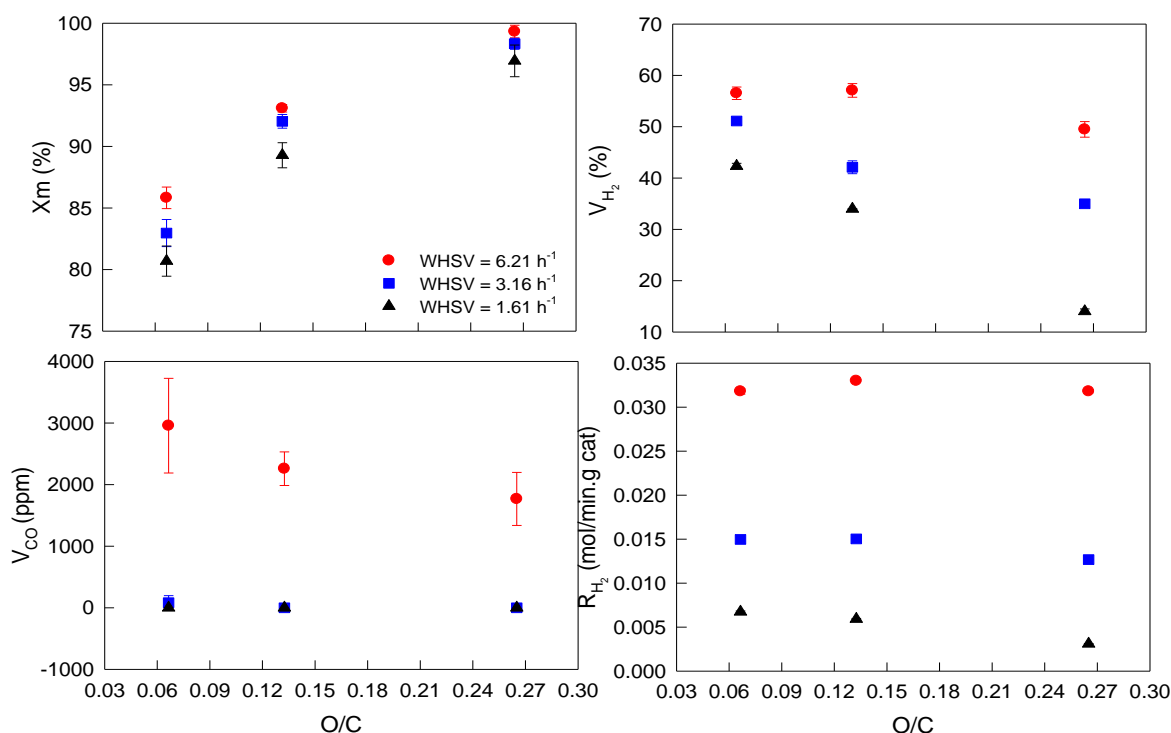


Figure 5. Cu/ZnO/Al₂O₃/Cr₂O₃/CeO₂ (15/15/2.5/1.25/1.25 mol%), EC sol, washcoat method, un-set pH (0.4), stirring 500 rpm (5 h), drying 50 °C (2 h), catalyst weight = 0.5 mg, W/M = 1.2, O/C = 0.07-0.27, WHSV = 1.60-6.21 h⁻¹, reaction temperature = 200 °C.

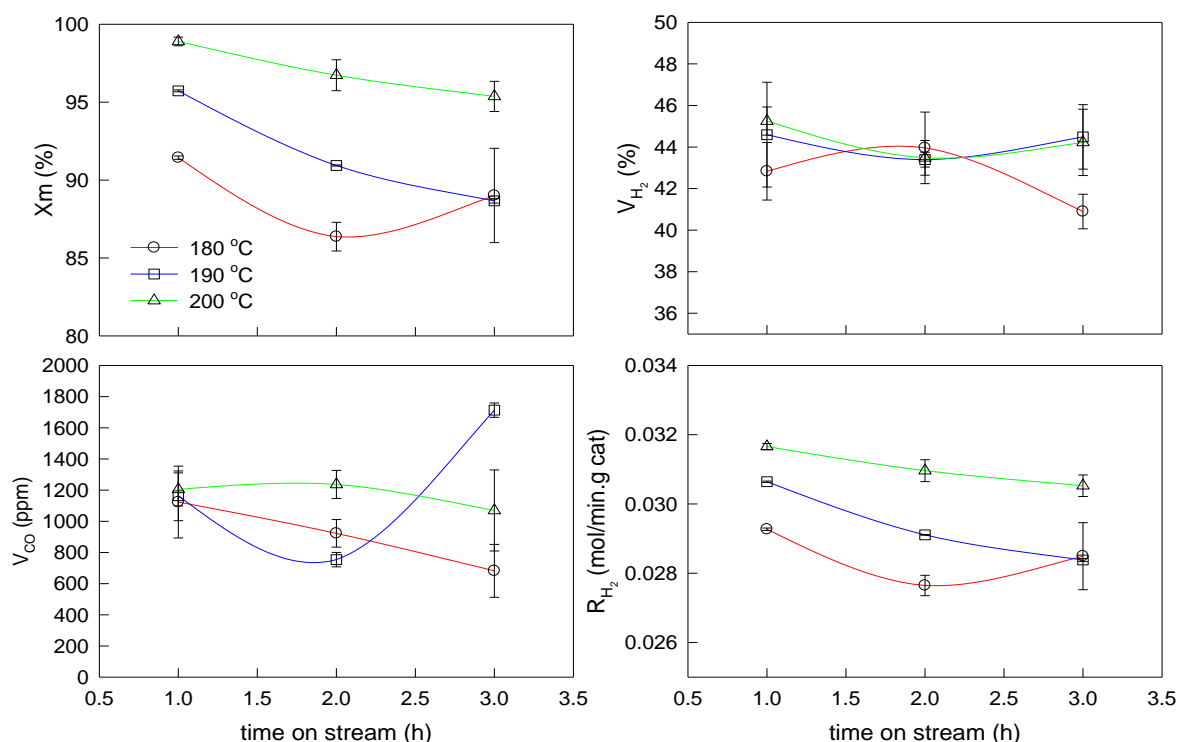


Figure 6. Cu/ZnO/Al₂O₃/Cr₂O₃/CeO₂ (15/15/2.5/1.25/1.25 mol%), EC sol, washcoat method, Un-set pH (0.4), stirring 500 rpm (5 h), drying 50 °C (2 h), catalyst weight = 0.5 mg, W/M = 1.2, O/C = 0.27, WHSV = 6.23 h⁻¹, Reaction temperature = 180-200 °C

with increasing molar ratio of O/C. However that the hydrogen production rate increases with decreasing molar ratio of O/C. Optimum operation condition was O/C about 0.27, WHSV about 6.21 h⁻¹. Reaction temperature about 200 °C is a optimum condition to get a good result.

Acknowledgement

The authors would like to thank the National Science Council of Taiwan for financially supporting this research under grant numbers NSC 100-2221-E-155-037-MY2.

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